

Study on Epoxy Resins Modified by Polycarbonate Polyurethanes

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ABSTRACT: In this article, the structure and properties of the epoxy resin (EP) modified by polyurethane (PU) prepolymers were studied. The three types of polyurethane prepolymers, namely, polycarbonate-type PU (TPC), polyether-type PU, and polycarbonate-polyether-type PU were employed. The samples were analyzed by means of an infrared spectrometer, a differential scanning calorimeter, a scanning electron microscope, a transmission electron microscope, a scanning tunnel microscope, and a thermal gravimeter. The results show that the EP modified by TPC is of excellent thermal resistance and mechanical properties. Specifically, when the ratio of PU to EP is 10/100 (wt/wt), optimal properties are achieved. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 887–893, 1998

Key words: epoxy resin; polycarbonate; polyurethane; modification

INTRODUCTION

Epoxy resins (EP) are an important class of thermosetting materials and chiefly used as adhesives; as products in the building industry; as components for casting, potting, and encapsulation; in filament winding; and as protective coatings and as molding compounds since they were synthesized late in the 1930s. Recently, considerable interest has been focused on the modification of EP because of their brittleness, low elongation at break, and poor impact strength. The most effective modification method of EP is to blend EP with other polymers, such as liquid rubber, butadiene–acrylonitrile rubber, organosilicon polymer, nylon, phenol formaldehyde resin, polysulfone, or polyurethane (PU). Polyether-, polyester-, castor oil-, and polybutadiene-type PU are often used as modifiers.^{1–3} In this work, the objective was to develop a new type of PU-modified EP (PU–EP) by reacting the EP

with the PU, which was synthesized with toluylene diisocyanate (TDI), poly(ether) diol (N-210), and poly(hexamethylene) carbonate diol (PC-210). The structure, mechanical properties, and thermal resistance of the products were studied so that the PU–EP of excellent comprehensive properties was obtained.

EXPERIMENTAL

Materials

Materials used in this study include TDI, PC-210, N-210, epoxy resin (E-44), 3,3'-dichloro-4-4'-diamino-diphenylmethane (MOCA), and 2,4,6-tri(dimethylaminomethyl) phenol (DMP-30). PC-210 was prepared in our own laboratory. N-210 was supplied by the Jin-Ling Petroleum Chemical Factory II. Epoxy resin was supplied by the Tianjin Jin-Dong Petroleum Chemical Factory. MOCA, DMP-30 and other chemicals were all purchased from the Shanghai Chemical Reagent Co.

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Table I PU Prepolymers Incorporated in the Study of Epoxy Resins

PU Name	NCO/ OH (mol/mol)	PC-210/ N-210 (g/g)	NCO Percentage (%)
TPC-2101	1.2	100/0	1.3
TPC-2102	1.5	100/0	2.6
TPC-2103	1.8	100/0	4.1
TPC-2104	2.0	100/0	5.2
TPC-2105	2.3	100/0	6.0
TNPC-2101	1.5	70/30	2.5
TNPC-2102	1.5	50/50	2.6
TNPC-2103	1.5	30/70	2.6
TNPC-2104	1.5	0/100	2.7

Preparation of PU Prepolymers

Nine kinds of PU prepolymers with isocyanate end group were prepared from TDI, PC-210, and N-210. The prepolymers prepared are shown in Table I.

Preparation of Specimens

PU-EP was prepared with two components, components I and II. The former includes PU prepolymer and MOCA dissolved by polar solvent, and the latter includes EP and DMP-30. The specimens were made as follows. Component I was dissolved in xylene, and a definite amount of compo-

nent II was added. Then the solvent was evaporated off. Finally, the samples were cured at 110°C for 6 h and then cooled to ambient temperature.

Measurement of Mechanical Properties

The impact strength was measured by use of an XCL-40 Charpy Impact Machine Tester according to GB1043-79. The adhesion shearing strength was measured by using an LJ-500A Tensile Testing Machine (Qing-Shan Testing Machine Plant) according to GB7124-86. The tensile strength was measured by using a ZLD-50 Electronic Instron Tensile Strength Tester (Chang-Chun Testing Machine Plant II) according to GB2568-21. Five samples were tested in each case, and the average value was obtained. All the tests were performed under ambient temperature in the order of $25 \pm 2^\circ\text{C}$.

Infrared Spectroscopy Investigations

Infrared (IR) spectrographs were recorded by means of a NICOLET 5DX Infrared Spectrometer using KBr coating sheet technology.

Microscopy Investigations

Scanning electron micrographs were obtained using an HITACHI X-650 Scanning Electron

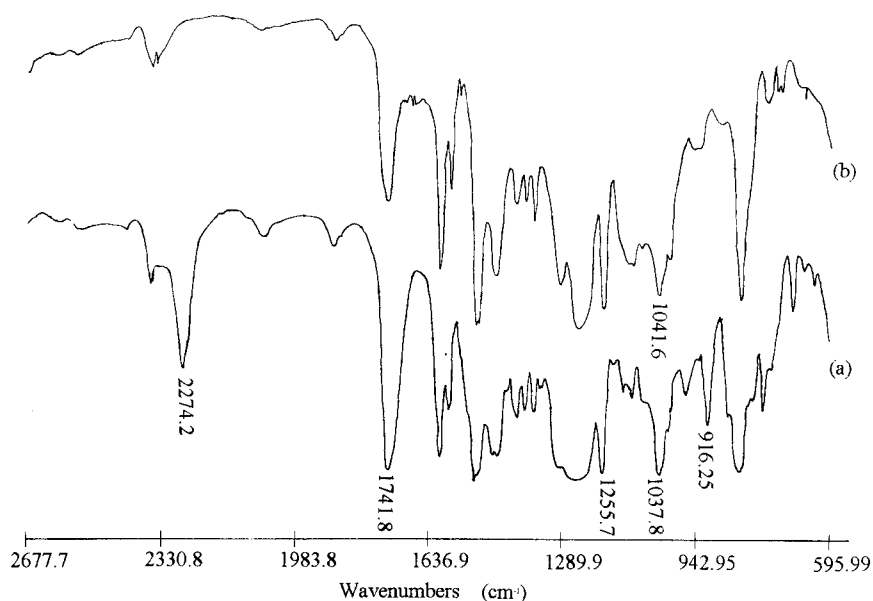


Figure 1 IR spectrographs of the PU-EP system without MOCA (a) at the beginning and (b) at the end.

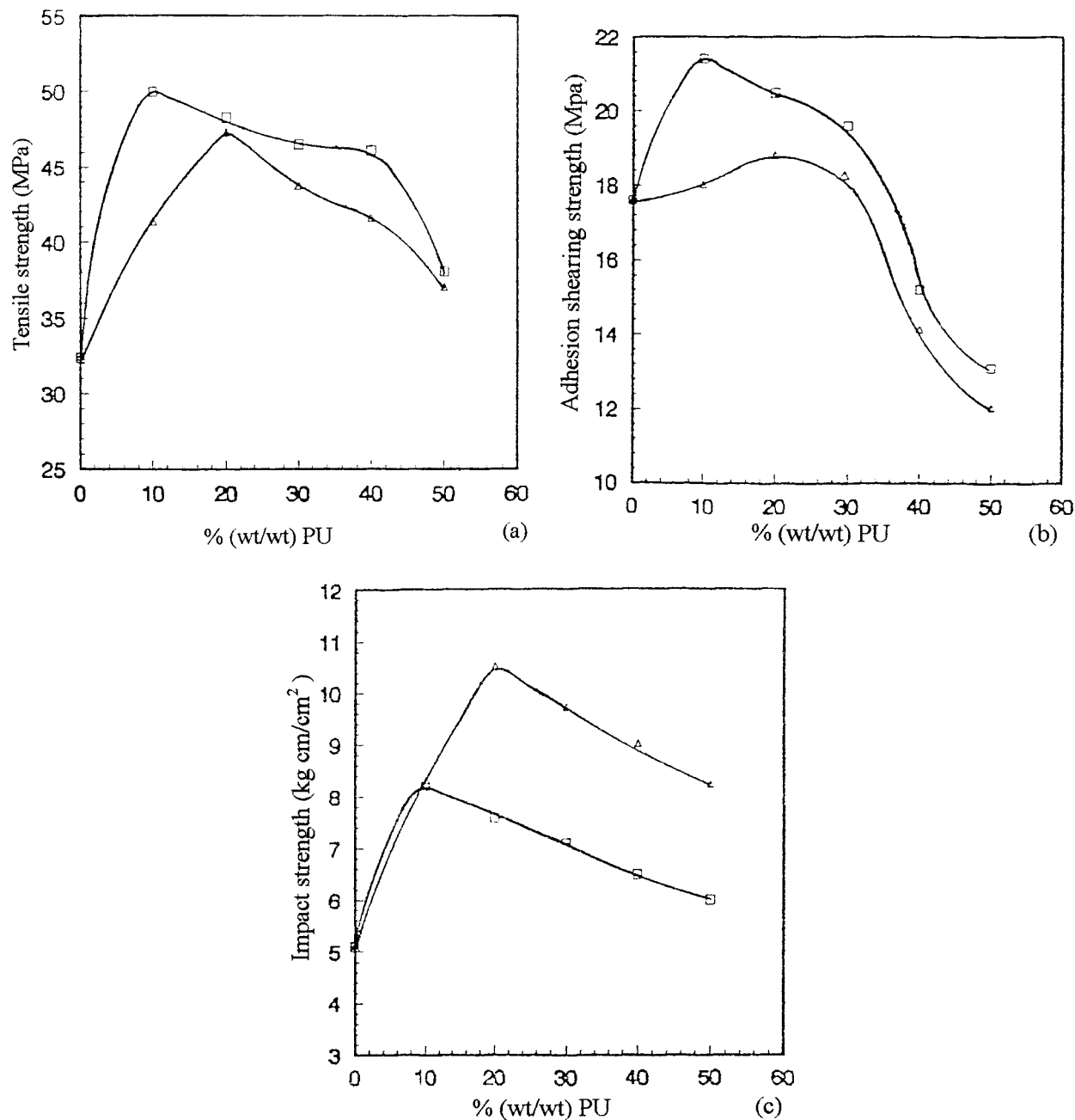


Figure 2 Effect of PU content on (□) TPC-2101-E-44 and (△) TNPC-2103-E-44: (a) tensile strength, (b) adhesion shearing strength, and (c) impact strength.

Microscope (SEM). All samples were sputter-coated with gold before SEM examination. Transmission electron micrographs were obtained using a Philips 400ST Transmission Electron Microscope (TEM). All samples were soaked and dyed in 2% OsO₄ solution at 36°C for 72 h, then cured and buried with epoxy resin, and finally microtomed into sheets before TEM examination. The surface of samples was tested by an AUTOPROBE Scanning Tunnel

Microscope (STM) made by Park Scientific Instrument.

Differential Scanning Calorimetry Measurement

Differential Scanning Calorimetry (DSC) measurement was conducted using a DSC instrument (Perkin-Elmer, DSC-2C). All samples were quenched in liquid nitrogen and dried previously. The samples were heated to 250°C at a stepping-

up rate of 20°C/min in a nitrogen atmosphere to obtain the heating curves.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was made with a TG-1 Thermal Gravimetric Analyzer at a stepping-up rate of 15°C/min.

RESULTS AND DISCUSSION

Infrared Analysis

Figure 1 shows IR spectrographs of the PU-EP without MOCA, both at the beginning and at the end of the reaction. It can be seen that the absorbance of the isocyanate group at 2274.2 cm^{-1} and the absorbance of the epoxy group at 916.25 cm^{-1} exist at the beginning of the reaction, but they both disappear, while the absorbance of the secondary hydroxy group in the EP become smaller, and the absorbance region changed from 1037.8 to 1041.6 cm^{-1} at the end of the reaction. It proves that the isocyanate group reacted with the hydroxy group. Besides, the absorbance of carbonate group at 1741.8 and 1255.7 cm^{-1} hardly varies during the reaction.

Mechanical Testing

The mechanical properties of the PU-EP are greatly influenced not only by the content and type of PU but also by the ratio of isocyanate group to hydroxy group ($R_{\text{NCO/OH}}$) (mol/mol) in the PU.

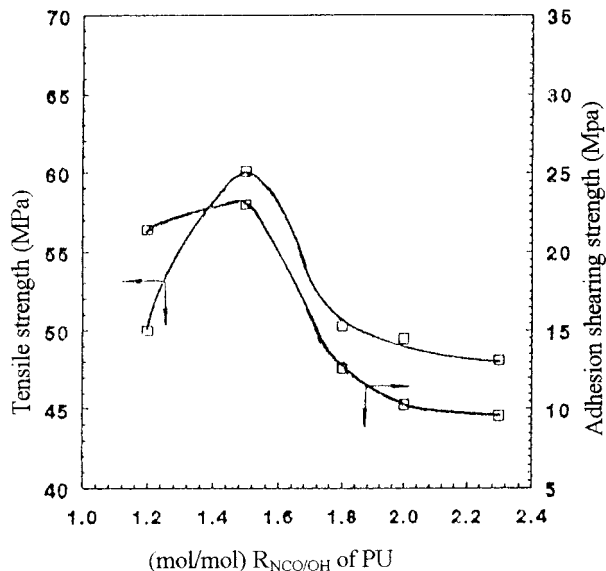


Figure 3 Effect of the $R_{\text{NCO/OH}}$ of PU.

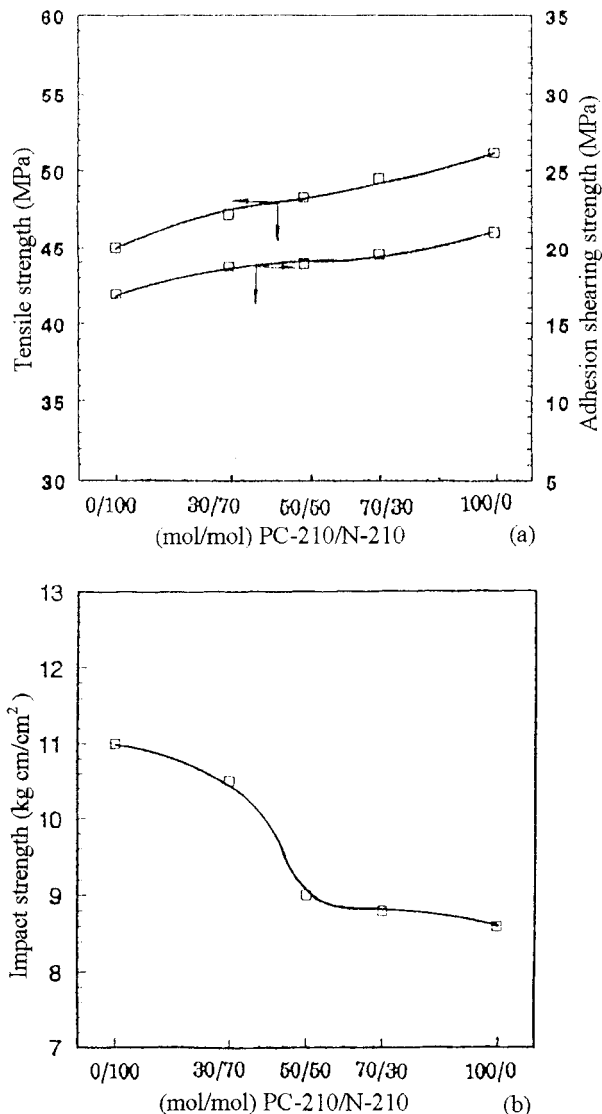


Figure 4 Effect of the ratio of PC-210 to N-210 in PU: (a) tensile strength and adhesion shearing strength and (b) impact strength.

Effect of PU Content

Figure 2 shows the effect of PU content on mechanical properties. It can be seen that the mechanical properties of the PU-EP increase greatly on adding a small amount of PU. The max-

Table II T_g of PU-EP

Samples (TPC-2102-E-44)	T_g (°C)
0/100	86.0
10/100	81.6
50/100	42.7 95.1

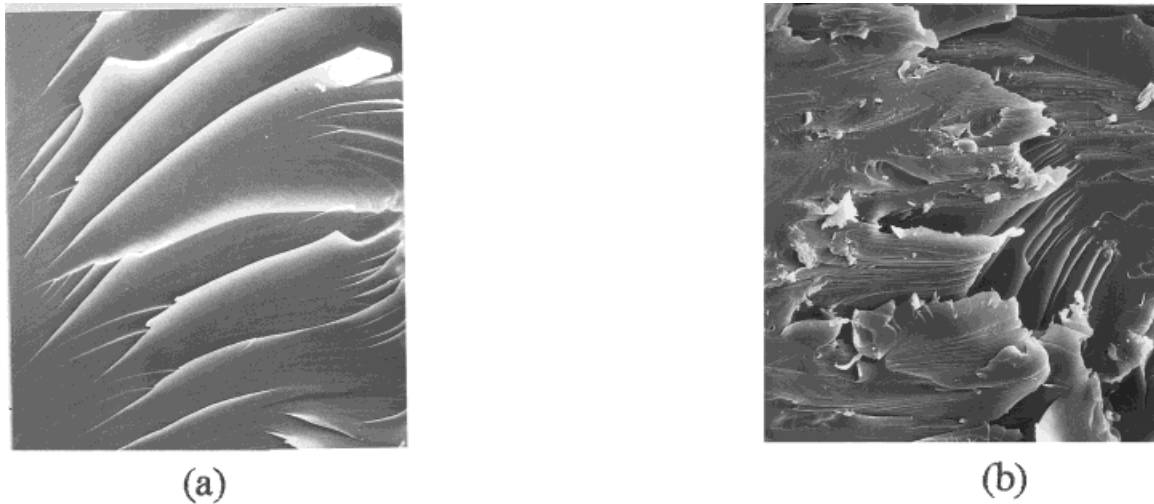


Figure 5 SEM micrographs of the fracture surface of EP: (a) unmodified EP and (b) TPC-modified EP (original magnification $\times 500$).

imum values of mechanical properties are obtained at the ratio 10/100 (PU–EP) for the TPC and at the ratio 20/100 (PU–EP) for the TNPC.

Effect of $R_{\text{NCO/OH}}$

To investigate the effect of $R_{\text{NCO/OH}}$ in PU on mechanical properties, the values of $R_{\text{NCO/OH}}$ range between 1.2/1 and 2.3/1. It can be seen that the tensile strength and adhesion shearing strength increase obviously at a low $R_{\text{NCO/OH}}$ and show a progressive decrease with an increase in $R_{\text{NCO/OH}}$ above the ratio 1.5/1 (from Fig. 3). When $R_{\text{NCO/OH}}$

is low, molecular chains are not apt to slip due to high molecular weight and intermolecular Van Der Walls force so that the tensile strength obviously increases. With an increase in $R_{\text{NCO/OH}}$, the molecular weight of PU decreases, but the crosslink density increases. Under tensioning, the initiation of the fracture occurs on the sites of stress concentration. As a result, the tensile strength and adhesion shearing strength of the PU–EP show a decreasing trend at above $R_{\text{NCO/OH}}$ of 1.5/1. Moreover, the excessive crosslinking results in microphase separation and indstructing the regularity of PU molecular chains, so the adhesion shearing strength decreases.

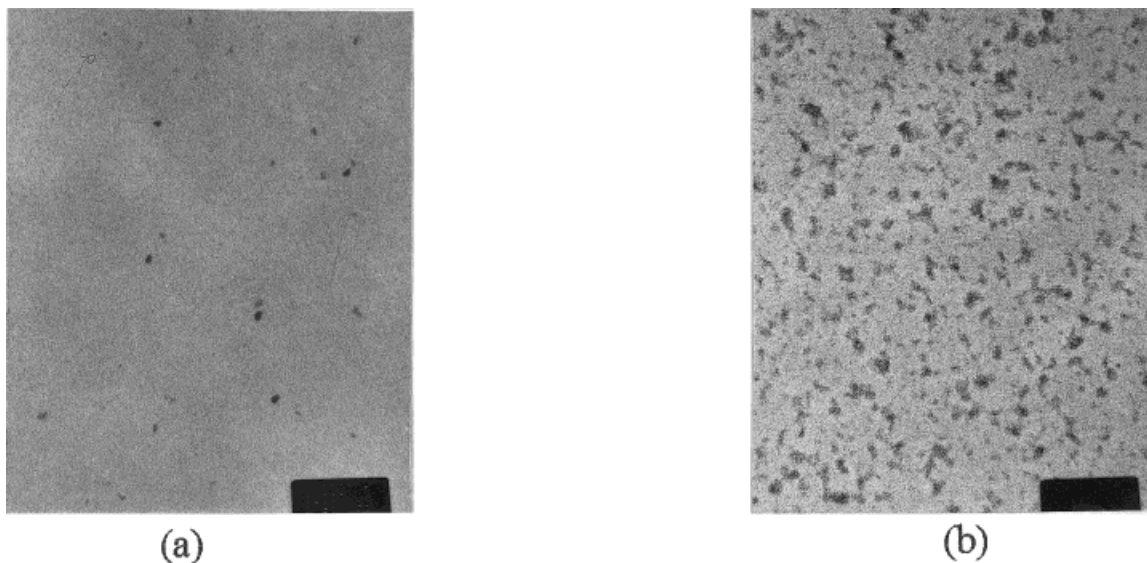


Figure 6 TEM micrographs of the etched surface for PU–EP: (a) TPC–EP (10/100) and (b) TPC–EP (50/100) (original magnification $\times 10^5$).

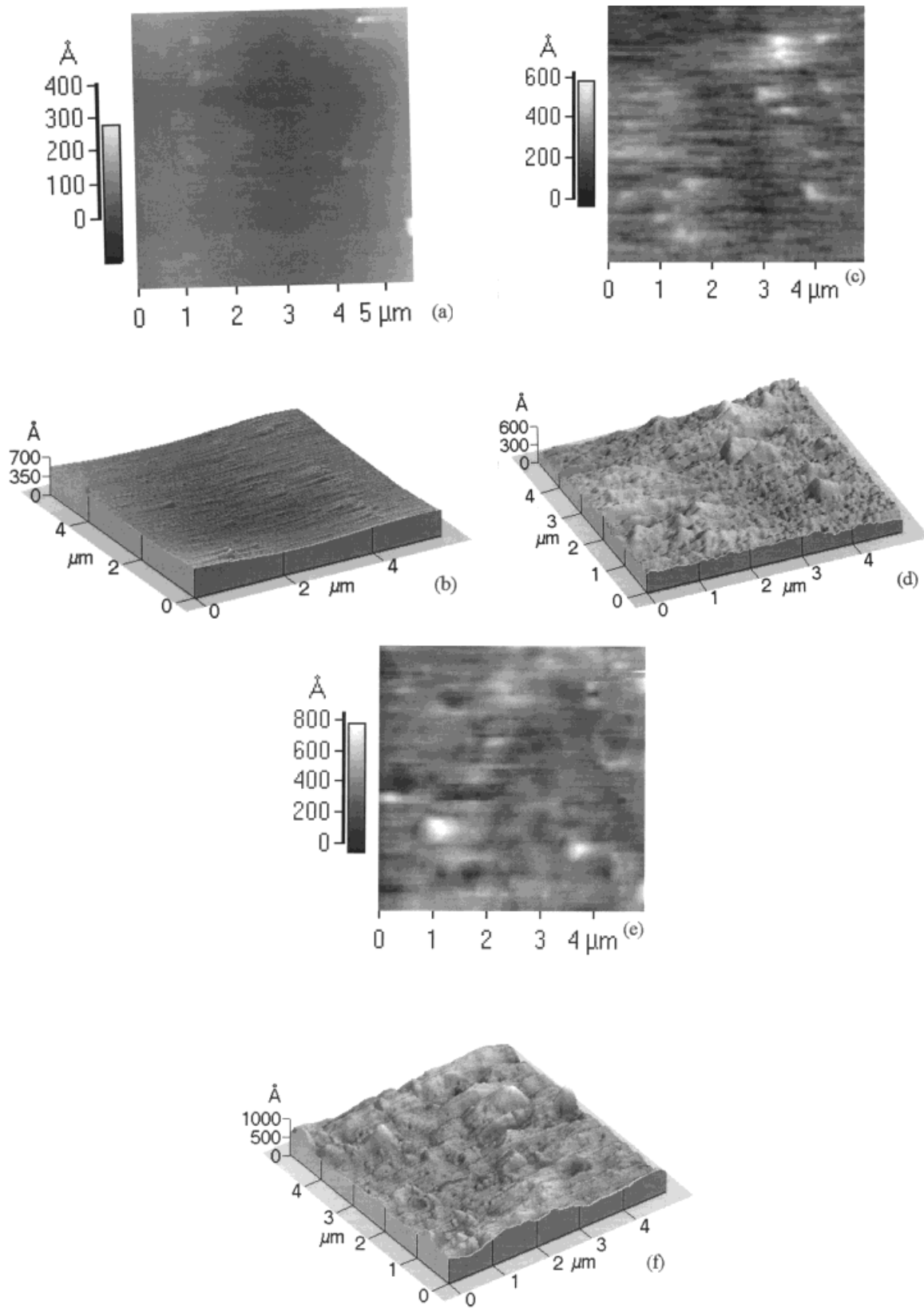


Figure 7 STM micrographs of the surface for PU-EP: (a) and (b) unmodified EP; (c) and (d) PU-EP (10/100); (e) and (f) PU-EP (50/100) [(a), (c), and (e) are plane micrographs; (b), (d), and (f) are stereo micrographs].

Table III Thermal Property Parameters of PU-EP

Samples	Starting Decomposing Temperature (°C)	Half Weight Loss Temperature (°C)	Remaining Percentage at 600°C (%)
Unmodified EP	113	426	17.4
TPC-2102-E-44 (10/100)	175	462	28.2
TPC-2102-E-44 (30/100)	120	420	15.1
TNPC-2101-E-44 (20/100)	166	434	8.1

Effect of Type of PU

The samples were prepared with TNPC-210 and E-44 at the ratio of 20/100. Figure 4(a) and (b) show that the tensile strength and adhesion shearing strength of TNPC-210-E-44 increase with an increase of the PC-210 component in PU, which was attributed to the strong polar carbonate group and high regular hexamethylene group. But the impact strength decreases because the ether bonds make molecular chains flexible.

DSC

The glass transition temperature (T_g) was obtained from measurement of the completely cured material (Table II). It can be seen that the TPC-EP is best compatible at the ratio 10/100 (TPC-EP). In this system, the amine group of MOCA react predominantly with the isocyanate group of the PU and then react with the epoxy group of the EP, which results in the formation of the PU-EP graft copolymer.⁴ With an increase of the PU content, two glass transition temperatures appear, which corresponds to phase separation.

Microscopy Investigations

An SEM was used to investigate the morphology of the PU-EP. Figure 5(a) is the SEM micrograph of a fracture surface of the unmodified EP. It can be seen that the fracture surface of E-44 is sleek. It shows a typical brittle fracture morphology. Figure 5(b) shows that the fracture surface of modified EP (E-44) is a fracture morphology of reinforced plastics.

Figure 6 show TEM micrographs of the etched surface for the PU-EP. It can be seen that from Figure 6(a), the PU particles disperse uniformly in EP matrix and their size, shape, and distribution vary tremendously [compared with Fig. 6(b)].

Figure 7(a)-(f) show STM micrographs of the surface for the PU-EP, which exhibit that the quantity and height of bulges increase and that

cavities appeared with an increase of the PU content. These reveal that the PU-EP achieves excellent compatibility at the ratio 10/100. It is consistent with Figure 2.

TGA

The modified EP has higher thermal resistance than the unmodified EP. TPC-210-E-44 achieves optimal properties when the ratio of TPC-210 to E-44 is 10/100 (Table III) because of the intermolecular hydrogen bonds of PU, which improve cohesion force; strong polar carbonate group; and high regular soft segments, which form close-packed structure. In addition, their thermal resistance varies with the PU content for the same type of PU. When the ratio of PU to EP is 10/100, the optimal properties achieve.

CONCLUSION

1. The graft reaction occurs in the PU-EP.
2. The brittleness of EP is improved, and the fracture surface of the PU-EP exhibits a fracture morphology of reinforced plastics.
3. The mechanical properties and thermal resistance of EP can be improved greatly on adding a small amount of TPC.
4. The mechanical properties and thermal resistance of EP are optimum at the ratio 10/100 (PU-EP).
5. $R_{\text{NCO/OH}}$ of PU has a great effect on the mechanical properties.

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